Iron and nickel doped CoSe2 as efficient non precious metal catalysts for oxygen reduction

Beibei Yu  
*Hubei University*

Jiayi Jin  
*Hubei University*

Huinmin Wu  
*Hubei University*, hw267@uow.edu.au

Shengfu Wang  
*Hubei University*

Qinghua Xia  
*Hubei University*

See next page for additional authors
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Keywords
precious, metal, catalysts, iron, oxygen, nickel, reduction, doped, cose2, efficient, non

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Authors
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Iron and nickel doped CoSe$_2$ as efficient non precious metal catalysts for oxygen reduction

Beibei Yu$^{1}$, Jiayi Jin$^{1}$, Huimin Wu*,$^{1}$, Shengfu Wang$^{1}$, Qinghua Xia$^{1}$, Huakun Liu**,$^{2}$

$^{1}$Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials & Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Ministry of Education & College of Chemistry & Chemical Engineering, Hubei University, Wuhan 430062, PR China

$^{2}$Institute for Superconducting & Electronic Materials, School of Mechanical, Materials and Mechatronics Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

Abstract: Iron and nickel doped CoSe$_2$ were prepared by solvothermal method, and they were proved to be ternary chalcogenides by series of physical characterization. The effects of the iron and nickel contents on the oxygen reduction reaction were investigated by electrochemical measurements, and the highest activities were obtained on Co$_{0.7}$Fe$_{0.3}$Se$_2$ and Co$_{0.7}$Ni$_{0.3}$Se$_2$, respectively. Both Co$_{0.7}$Fe$_{0.3}$Se$_2$ and Co$_{0.7}$Ni$_{0.3}$Se$_2$ presented four-electron pathway. Furthermore, Co$_{0.7}$Fe$_{0.3}$Se$_2$ exhibited more positive cathodic peak potential (0.564 V) and onset potential (0.759 V) than these of Co$_{0.7}$Ni$_{0.3}$Se$_2$ (0.558V and 0.741V). And Co$_{0.7}$Fe$_{0.3}$Se$_2$ displayed even superior stability and better tolerance to methanol, ethanol and ethylene glycol crossover effects than the commercial Pt/C (20 wt% Pt).

Keywords: Non-noble metal catalyst; Chalcogenide; Electrocatalysis; Oxygen reduction reaction

* Corresponding author. Tel.: 86 18971479006; Fax: 86 27 88663043.
E-mail address: whm267@hubu.edu.cn

** Corresponding author. E-mail address: hua_liu@uow.edu.au
1. Introduction

Nowadays, non-precious metal-based electrocatalysts have exhibited promising activities towards oxygen reduction reaction (ORR) [1-4]. Among them, cobalt based selenides (CoSe\textsubscript{x}) are attracting enormous interest as new ORR electrocatalysts. For example, CoSe\textsubscript{2}/C obtained by Feng et al. [5, 6] showed superior electrocatalytic activity towards ORR with an open circuitry potential of 0.81 V in 0.5 M H\textsubscript{2}SO\textsubscript{4}, and higher methanol tolerance than that of Pt/C. Susac et al. [7] exhibited that cobalt-selenium (Co-Se) with varying content of Se obtained by magnetron sputtering and chemical methods indicated a electrocatalytic activity towards ORR in an acidic electrolyte.

However, the ORR activities of these materials are still far from proton exchange membrane fuel cells’ practical applications [8-11]. To further improve electrocatalytic activity, doping of transition metal is crucial to the Co-based chalcogenides. Zhao et al. [12] exhibited the tungsten doped Co-Se electrocatalysts synthesized by decarbonylation of carbonyl compounds in 1,6-hexanediol solvent, and indicated high ORR electrocatalytic activity in 0.5 M H\textsubscript{2}SO\textsubscript{4}. Nanosized particles of Ru\textsubscript{x}Fe\textsubscript{y}Se\textsubscript{z} were prepared by Solorza-Feria [13] showed higher electrocatalytic activity towards ORR than that of the Ru\textsubscript{x}Se\textsubscript{y}.

In order to enhance ORR electrocatalytic activity, two series of ternary non-noble metal chalcogenides were synthesized in this work. The electrocatalytic activity towards ORR and stability of the chalcogenides were investigated in 0.5 M H\textsubscript{2}SO\textsubscript{4}. Furthermore, the relationships between the content of doping transition metals and electrocatalytic activity were investigated.

2. Experimental
2.1. Electrocatalyst synthesis

All chemicals were purchased from Sigma-Aldrich.

\( \text{Co}_{x} \text{Fe}_{1-x} \text{Se}_2 \) \((x = 0.9, 0.8, 0.7, 0.6, 0.5)\) were obtained via a solvothermal method. Briefly, 0.291g cobalt nitride hexahydrate \((\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O})\) and different iron \((\Pi)\) sulfate heptahydrat \((\text{FeSO}_4 \cdot 7\text{H}_2\text{O})\) (Table S1) were dissolved in 30 mL diethylenetriamine \((\text{DETA})\) and deionized water \((\text{DIW})\) \((V_{\text{DETA}}/V_{\text{DIW}}= 2:1)\). Then, 0.591g sodium selenite \((\text{Na}_2\text{SeO}_3)\) and 8.5 mL hydrazine hydrate \((\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O})\) were added into the solution, and stirred for 30 min. Finally, the mixture was transferred into an autoclave and treated at 140°C for 24 h.

\( \text{Co}_{x} \text{Ni}_{1-x} \text{Se}_2 \) \((x = 0.9, 0.8, 0.7, 0.6, 0.5)\) were prepared by the similar method, only using nickel nitride hexahydrate \((\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O})\) (Table S2) instead of \(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}\). \(\text{CoSe}_2\) was prepared with no addition of \(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}\) [14].

2.2. Characterization

X-ray diffraction \((\text{XRD})\) experiments were carried out on a GBC MMA X-ray diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy \((\text{XPS})\) was performed by an ESCALAB 250Xi device. Scanning electron microscopy \((\text{SEM})\) with energy-dispersive X-ray spectroscopy \((\text{EDX})\) attachment \((\text{JSM6510LV})\) was used to observe the morphological and chemical composition analyses. The specific surface area was measured by a Quantachrome iQ-MP nitrogen adsorption apparatus.

The ORR activities of all catalysts were obtained with a CHI 750E electrochemical workstation \((\text{CH Instrument Company, Shanghai, China})\). Pt wire and saturated calomel electrode as the counter and reference electrodes, respectively. Rotating disk electrode \((\text{RDE, 5 mm in diameter})\) loaded with various catalysts was used as the working electrodes. 5 mg catalyst was ultrasonically dispersed in 0.5 mL Nafion solution. Then, 10 \(\mu\text{L (0.1 mg catalyst)}\) suspension was transferred on the RDE. All
the potentials of this paper were reported with respect to reversible hydrogen electrode (RHE).

3. Results and discussion

3.1. Material characteristics

Fig. 1 (A) showed the XRD patterns of (a) Co$_{0.9}$Fe$_{0.1}$Se$_2$, (b) Co$_{0.8}$Fe$_{0.2}$Se$_2$, (c) Co$_{0.7}$Fe$_{0.3}$Se$_2$, (d) Co$_{0.6}$Fe$_{0.4}$Se$_2$ and (e) Co$_{0.5}$Fe$_{0.5}$Se$_2$, respectively. While Fig. 1 (B) showed the XRD patterns of (a) Co$_{0.9}$Ni$_{0.1}$Se$_2$, (b) Co$_{0.8}$Ni$_{0.2}$Se$_2$, (c) Co$_{0.7}$Ni$_{0.3}$Se$_2$, (d) Co$_{0.6}$Ni$_{0.4}$Se$_2$ and (e) Co$_{0.5}$Ni$_{0.5}$Se$_2$, respectively. The observed diffraction peaks could be indexed to CoSe$_2$ (200), (210), (220), (311), (123), (400), (331) and (024) (JCPDS No. 09-234). No additional peaks of other phases had been observed, confirming the substitution of Fe or Ni in CoSe$_2$ lattice [15]. The intensity of the peaks reduced with the doping concentration increasing, which indicated the loss of crystallinity due to lattice distortion and smaller crystallite size [15]. However, the ternary Co-Fe-Se or Co-Ni-Se phase had not been investigated. These could due to the phases present in a very small nanocrystal, or overlap of diffraction peaks from CoSe$_2$ phase and Co-Fe-Se or Co-Ni-Se phase [16, 17]. Among these materials, Co$_{0.7}$Fe$_{0.3}$Se$_2$ and Co$_{0.7}$Ni$_{0.3}$Se$_2$ showed better catalytic activity towards ORR than others according to Fig. S2.
Fig. 1 (A) XRD patterns of (a) Co$_{0.9}$Fe$_{0.1}$Se$_2$, (b) Co$_{0.8}$Fe$_{0.2}$Se$_2$, (c) Co$_{0.7}$Fe$_{0.3}$Se$_2$, (d) Co$_{0.6}$Fe$_{0.4}$Se$_2$ and (e) Co$_{0.5}$Fe$_{0.5}$Se$_2$, (B) XRD patterns of (a) Co$_{0.9}$Ni$_{0.1}$Se$_2$, (b) Co$_{0.8}$Ni$_{0.2}$Se$_2$, (c) Co$_{0.7}$Ni$_{0.3}$Se$_2$, (d) Co$_{0.6}$Ni$_{0.4}$Se$_2$ and (e) Co$_{0.5}$Ni$_{0.5}$Se$_2$. XPS spectra of Co$_{0.7}$Fe$_{0.3}$Se$_2$ in the (C) Co 2p, (D) Fe 2p, and (E) Se 3d regions.

The XPS of Co$_{0.7}$Fe$_{0.3}$Se$_2$ showed that it mainly consisted of Co, Fe, and Se elements. Apparently, the binding energy of each element revealed a shift compared with their pure elements. The binding energies of Co 2p$_{3/2}$ (780.1 eV, Fig. 1 (C)) and Fe 2p$_{3/2}$ (711.6 eV, Fig. 1 (D)) were much higher than binary chalcogenides such as
CoSe$_2$ ($\text{Co } 2p_{3/2} = 778.7 \text{ eV}$) [18, 19] and iron diselenide ($\text{FeSe}_2$, $\text{Fe } 2p_{3/2} = 707.2 \text{ eV}$) [20]. However, Se $3d_{5/2}$ (Fig. 1 (E)) shifted to more negative binding energy than CoSe$_2$ (Se $3d_{5/2} = 54.4 \text{ eV}$) [18, 19]. And the relative amount of Se oxide (4.06%) was formed at the Co$_{0.7}$Fe$_{0.3}$Se$_2$ surface based on XPS analyses. However, the oxide is too small amount that it cannot be detected by XRD. The changes in binding energies for these elements can be explained by the fact that selenium is more electronegative than iron or cobalt. Charge transfer from cobalt and iron to selenium could lead to the chemical shift. So, cobalt and iron moved to positive binding energy, while selenium moved to negative binding energy. The results suggested it was a ternary chalcogenide [21]. Meanwhile, The XPS spectra of Co$_{0.7}$Ni$_{0.3}$Se$_2$ was shown in Fig. S3. The binding energies of Co $2p_{3/2}$ (780.3 eV, Fig. S3 (A)) and Ni $2p_{3/2}$ (855.1 eV, Fig. S3 (B)) were much higher than CoSe$_2$ (Co $2p_{3/2} = 778.7 \text{ eV}$) and nickel diselenide ($\text{NiSe}_2$, Ni $2p_{3/2} = 853.1 \text{ eV}$) [22, 23]. And, selenium shifts to negative binding energy of Se $3d_{5/2}$ (Fig. S3 (C)) compared to CoSe$_2$ (Se $3d_{5/2} = 54.4 \text{ eV}$), indicating that it also was a complete ternary chalcogenide. The relative amount of Se oxide was 2.23%.

SEM of Co$_{0.7}$Ni$_{0.3}$Se$_2$ and Co$_{0.7}$Fe$_{0.3}$Se$_2$ were shown in Fig.2 (A) and (B), respectively. Co$_{0.7}$Ni$_{0.3}$Se$_2$ revealed a fluffy morphology. However, the Co$_{0.7}$Fe$_{0.3}$Se$_2$ was mainly composed of a huge amount of homogeneous sphere-like shaped particles, so maybe had bigger surface areas. Meanwhile, the specific surface areas of Co$_{0.7}$Ni$_{0.3}$Se$_2$ and Co$_{0.7}$Fe$_{0.3}$Se$_2$ were measured to be 35.6 and 43.5 m$^2$·g$^{-1}$, respectively. According to report [24], the high specific surface areas could contribute to create abundant active sites, which made them more accessible. Maybe different contents of doped iron or nickel could affect the morphology (Fig. S4). Fig.2 (a) and (b) represented the EDX of Co$_{0.7}$Ni$_{0.3}$Se$_2$ and Co$_{0.7}$Fe$_{0.3}$Se$_2$, respectively. The results of EDX (Table 1) were consistent with XPS, which were very close to the design
results.

![Fig. 2 SEM and EDX images of (A, a) Co_{0.7}Ni_{0.3}Se_2 and (B, b) Co_{0.7}Fe_{0.3}Se_2.](image)

Table 1 XPS and EDX analyses of Co_{0.7}Fe_{0.3}Se_2 and Co_{0.7}Ni_{0.3}Se_2.

<table>
<thead>
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<th>Sample</th>
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<th></th>
<th>EDX (at. %)</th>
</tr>
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<td></td>
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<td>Fe</td>
<td>Ni</td>
</tr>
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<td>5.03</td>
<td>--</td>
</tr>
<tr>
<td>Co_{0.7}Ni_{0.3}Se_2</td>
<td>4.47</td>
<td>--</td>
<td>2.06</td>
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</table>

3.2. Electrochemical characterization

Linear sweep voltammetry (LSV) measurements were shown in Fig. 3 (A). The onset potential (E_{ORR}) was defined as potential at which the current density was equal to zero. And the half-wave potential (E_{1/2}), when the current density was equal to half of the limiting diffusion current density, was extracted from the polarization curve.
The more positive $E_{\text{ORR}}$ and $E_{1/2}$ were, the better electrocatalytic activity towards ORR they showed [25]. Except for Pt/C, Co$_{0.7}$Fe$_{0.3}$Se$_2$ exhibited more positive $E_{\text{ORR}}$ and $E_{1/2}$ compared with CoSe$_2$ and Co$_{0.7}$Ni$_{0.3}$Se$_2$, suggesting a much better ORR activity, and the parameters were listed in Table 2. Previous reports showed that the doping of Fe on Co-based chalcogenides could improve the constitution and stabilization of the catalytically active species, resulting in favorable ORR performance [26].

The durabilities of CoSe$_2$, Co$_{0.7}$Ni$_{0.3}$Se$_2$ and Co$_{0.7}$Fe$_{0.3}$Se$_2$ were also analyzed by Cyclic voltammograms (CVs), and selected the current densities of different cycles to draw the Fig. 3 (B). Obviously, Co$_{0.7}$Fe$_{0.3}$Se$_2$ and Co$_{0.7}$Ni$_{0.3}$Se$_2$ showed excellent long-term performance. Furthermore, the maximum current densities values of the Co$_{0.7}$Fe$_{0.3}$Se$_2$ were higher than those of the CoSe$_2$ and Co$_{0.7}$Ni$_{0.3}$Se$_2$. The electrochemical stability of the catalyst might be related to the amount of selenium on the CoSe$_2$. It had been reported that selenium can play a role in protecting the electrochemical oxidation of metals in chalcogenide compounds [27]. And the presence of Se oxide could also prevent dissolution in O$_2$-saturated 0.5 M H$_2$SO$_4$, which might contribute to its excellent stability [28]. At the same time, Fe or Ni doped the CoSe$_2$ increased adsorption/desorption of metals compounds associated with microporous structure [29, 30].

A series of LSV curves recorded from 100 to 2500 rpm were obtained in Fig. 3 (C). Koutecky-Levich (K-L) plots at different potentials showed good linearity (Fig. 3 (D)), revealing first-order reaction kinetics towards the concentration of dissolved oxygen [31]. The electron transfer number (n) could be calculated from the following K-L equations (1) [32], and n was calculated to be 4:

$$j^{-1} = j_k^{-1} + j_d^{-1} = j_k^{-1} + (B\omega^{1/2})^{-1}$$

where $j$, $j_d$ and $j_k$ were the measured, diffusion-limited and kinetic current densities, $\omega$
represented the electrode rotating rate. Co₀.₇Fe₀.₃Se₂, Co₀.₇Ni₀.₃Se₂ and Pt/C showed a
direct 4e⁻ reduction process towards ORR (Table 2) [33], while other CoₓFe₁ₓSe₂ and
CoₓNi₁ₓSe₂ (Fig. S5) with different iron or nickel contents exhibited a mixed
four-electron and two-electron reduction processes with H₂O₂ as the intermediate
agent. The corresponding values of 𝐯 and 𝑛 were shown in Fig. S6 (B, D). The
electronic structure of the transition metal was usually expressed by a percentage of d
orbital in the metal bond (d%). The higher value of d% was, the more electrons filling
in corresponding d energy band was, leading to less holes. The d% of the transition
metal in the order of Ni (40) > Co (39.7) > Fe (39.5). When the smaller values (d%) of
the metal (Fe) added to CoSe₂, the bigger d% of Co atoms was transferred to
smaller d% of the Fe atoms. Which increased the holes of Co, and improved the
adsorption rate of oxygen. Although the difference between iron and nickel was very
small, the d% of Ni was bigger than Co [34]. Therefore, the bonding ability of
Co₀.₇Fe₀.₃Se₂ was higher than that of Co₀.₇Ni₀.₃Se₂, implying Co₀.₇Fe₀.₃Se₂ presented
better ORR activity.

Fig. 3 (E) showed the tafel plots of the Co₀.₇Fe₀.₃Se₂, Co₀.₇Ni₀.₃Se₂ and CoSe₂
towards ORR. The 𝐯 and 𝑛 were calculated using K-L equation, Co₀.₇Fe₀.₃Se₂ exhibited a
highest value than that of Co₀.₇Ni₀.₃Se₂ and CoSe₂. The tafel slope (b) and transfer
coefficient (α) were listed in Table 2. The highest ORR activity of Co₀.₇Fe₀.₃Se₂ was
further supported by the smallest tafel slope of 110 mV/decade among CoSe₂,
CoₓFe₁ₓSe₂ and CoₓNi₁ₓSe₂ with different iron or nickel contents (Fig. S6 (A, C)).
Which indicated that the ORR on Co₀.₇Fe₀.₃Se₂ was controlled by the first electron
transfer process, similar to that of the Pt/C (Fig. S6 (E)) [35]. Moreover, the results
were comparable or even better than other catalysts in Table 2. It might be due to the
doped Fe increased the surface area, adsorption/desorption of metals compounds, and
electron transport between electrode substrate and electrolyte interface [29, 30].

Fig. 3 (A) LSV curves of Pt/C, CoSe₂, Co₀.₇Ni₀.₃Se₂ and Co₀.₇Fe₀.₃Se₂ in O₂-saturated 0.5 M H₂SO₄ at 1600 rpm and a scan rate of 10 mV s⁻¹. (B) The maximum current densities of CoSe₂, Co₀.₇Ni₀.₃Se₂ and Co₀.₇Fe₀.₃Se₂ recorded during repeated cycling by CVs. (C) LSV curves of the Co₀.₇Fe₀.₃Se₂ in O₂-saturated 0.5 M H₂SO₄ at different rotation rates. (D) K-L plots of Co₀.₇Fe₀.₃Se₂ at various potentials. (E) Tafel plots of CoSe₂, Co₀.₇Ni₀.₃Se₂ and Co₀.₇Fe₀.₃Se₂ at 1600 rpm. (F) LSV curves of Co₀.₇Fe₀.₃Se₂ in O₂-saturated 0.5 M H₂SO₄ containing CH₃OH (0-2 M), Co₀.₇Ni₀.₃Se₂ was shown in corresponding inset.

Table 2 Comparison of catalytic activity data with Co₃Feₓ/₀.₃Se₂, Co₃Niₓ/₀.₃Se₂, CoSe₂
Pt/C and other catalysts reported in the literature based ORR catalysts.

| Catalyst     | E_{ORR} | E_{1/2} | n  | -b | α  | |j| at 0.3V |
|--------------|---------|---------|----|----|----|---------|
| Co_{0.9}Fe_{0.1}Se_{2} | 0.740   | 0.576   | 3.3| 121| 0.625| 1.440   |
| Co_{0.8}Fe_{0.2}Se_{2} | 0.747   | 0.582   | 3.9| 117| 0.639| 1.722   |
| Co_{0.7}Fe_{0.3}Se_{2} | 0.759   | 0.584   | 4.0| 110| 0.645| 1.830   |
| Co_{0.6}Fe_{0.4}Se_{2} | 0.745   | 0.580   | 3.8| 119| 0.635| 1.672   |
| Co_{0.5}Fe_{0.5}Se_{2} | 0.737   | 0.573   | 3.2| 125| 0.622| 1.437   |
| Co_{0.9}Ni_{0.1}Se_{2} | 0.736   | 0.499   | 3.8| 117| 0.617| 1.777   |
| Co_{0.8}Ni_{0.2}Se_{2} | 0.739   | 0.552   | 3.9| 116| 0.626| 1.790   |
| Co_{0.7}Ni_{0.3}Se_{2} | 0.741   | 0.556   | 4.0| 111| 0.640| 1.827   |
| Co_{0.6}Ni_{0.4}Se_{2} | 0.733   | 0.489   | 2.8| 120| 0.558| 1.211   |
| Co_{0.5}Ni_{0.5}Se_{2} | 0.731   | 0.485   | 2.4| 121| 0.543| 1.036   |
| CoSe_{2}      | 0.708   | 0.560   | 3.9| 112| 0.638| 1.522   |
| Pt/C          | 0.934   | 0.760   | 4.0| 110| 0.847| 1.871   |
| W-Co-Se [21]  | 0.755   | -       | 2.0| 113| -    | -       |
| Ru_{x}Mo_{y}Se_{z} [38]| 0.740   | -       | 4.0| 116| 0.520| -       |
| Ru_{x}Cr_{y}Se_{z} [39]| 0.800   | -       | 4.0| 116| 0.510| -       |
| CoSe_{2}/C [5] | 0.720   | -       | -  | 125| -    | -       |
| Co_{7}Se_{8} [40]| 0.811   | -       | 3.9| 121| -    | -       |
| Fe_{3}O_{4}/ CoSe_{2} [41]| 0.760   | -       | 3.6| -  | -    | -       |

The satisfactory catalyst towards ORR should exhibit superior tolerance to the fuels (such as methanol, ethanol and ethylene glycol), which could penetrate the membrane from the anode [14]. We measured the LSV of Co_{0.7}Fe_{0.3}Se_{2} (Fig. 3 (F), S7 (C, E)), Co_{0.7}Ni_{0.3}Se_{2} (Fig. 3 (F) (inset), S7 (D, F)) and Pt/C (Fig. S7 (A, B, G)) in O_{2}-saturated 0.5 M H_{2}SO_{4} containing 0-2 M methanol, ethanol and ethylene glycol, respectively. Compared with CoSe_{2} [14], Co_{0.7}Fe_{0.3}Se_{2} and Co_{0.7}Ni_{0.3}Se_{2} showed little activity loss and had favorable tolerance to the methanol, ethanol and ethylene glycol. In contrast, there was an obvious decrease in the ORR activity of Pt/C, because of the
competitive reaction between oxygen reduction and methanol, ethanol and ethylene glycol oxidation [36, 37].

4. Conclusions

In summary, Fe and Ni doped CoSe$_2$ were successfully synthesized. The ORR catalytic activity of Co$_x$Fe$_{1-x}$Se$_2$ and Co$_x$Ni$_{1-x}$Se$_2$ catalysts changed with iron or nickel contents. As a result, Co$_{0.7}$Fe$_{0.3}$Se$_2$ demonstrated an excellent electroactivity and durability towards ORR, making it a promising non-noble metal electrocatalyst for full cells.

Acknowledgements

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The prepared materials corresponding to the precursors’ amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$

Table S1

The amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

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<th>Material number</th>
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<td>$\text{Co}<em>{0.5}\text{Fe}</em>{0.5}\text{Se}_2$</td>
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</table>

Table S2

The amounts of $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>Material number</th>
<th>$\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co}<em>{0.9}\text{Ni}</em>{0.1}\text{Se}_2$</td>
<td>0.032</td>
</tr>
<tr>
<td>$\text{Co}<em>{0.8}\text{Ni}</em>{0.2}\text{Se}_2$</td>
<td>0.073</td>
</tr>
<tr>
<td>$\text{Co}<em>{0.7}\text{Ni}</em>{0.3}\text{Se}_2$</td>
<td>0.125</td>
</tr>
<tr>
<td>$\text{Co}<em>{0.6}\text{Ni}</em>{0.4}\text{Se}_2$</td>
<td>0.194</td>
</tr>
<tr>
<td>$\text{Co}<em>{0.5}\text{Ni}</em>{0.5}\text{Se}_2$</td>
<td>0.291</td>
</tr>
</tbody>
</table>
**CVs, LSV and Nyquist plots of Co$_x$Fe$_{1-x}$Se$_2$ and Co$_x$Ni$_{1-x}$Se$_2**

Fig. S2 showed CVs, LSV, and Nyquist plots of Co$_x$Fe$_{1-x}$Se$_2$ and Co$_x$Ni$_{1-x}$Se$_2$ with different iron or nickel contents in O$_2$-saturated 0.5 M H$_2$SO$_4$. Obviously, the electrocatalytic activities of Co$_{0.7}$Fe$_{0.3}$Se$_2$ and Co$_{0.7}$Ni$_{0.3}$Se$_2$ were better than others.

![Diagram of CVs, LSV, and Nyquist plots](image)

Fig. S2 CVs and LSV curves of (A, C) Co$_x$Fe$_{1-x}$Se$_2$ and (B, D) Co$_x$Ni$_{1-x}$Se$_2$ with different iron or nickel contents in O$_2$-saturated 0.5 M H$_2$SO$_4$ at a scan rate of 10 mV s$^{-1}$. Nyquist plots of (E) Co$_x$Fe$_{1-x}$Se$_2$ and (F) Co$_x$Ni$_{1-x}$Se$_2$ with different iron or nickel contents in O$_2$-saturated 0.5 M H$_2$SO$_4$ at open potential, frequency range: 1-10$^6$ Hz.

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**XPS spectra of Co$_{0.7}$Ni$_{0.3}$Se$_2$**

Fig. S3 showed XPS spectra of the Co$_{0.7}$Ni$_{0.3}$Se$_2$. The binding energies of Co 2p$_{3/2}$ (780.3 eV, Fig. S3 (A)) and Ni 2p$_{3/2}$ (855.1 eV, Fig. S3 (B)) were much higher than CoSe$_2$ (Co 2p$_{3/2}$= 778.7 eV) and nickel diselenide (NiSe$_2$, Ni 2p$_{3/2}$= 853.1 eV). However, selenium shifts to negative binding energy of Se 3d$_{5/2}$ (Fig. S3 (C)) compared to CoSe$_2$ (Se 3d$_{5/2}$= 54.4 eV), indicating that it was a complete ternary chalcogenide.

![XPS Spectra](image)

Fig. S3 XPS spectra of Co$_{0.7}$Ni$_{0.3}$Se$_2$ in the (A) Co 2p, (B) Ni 2p and (C) Se 3d regions.
IVSEM of Co$_{0.9}$Fe$_{0.1}$Se$_2$, Co$_{0.5}$Fe$_{0.5}$Se$_2$, Co$_{0.9}$Ni$_{0.1}$Se$_2$ and Co$_{0.5}$Ni$_{0.5}$Se$_2$

Fig. S4 showed SEM of (A) Co$_{0.9}$Ni$_{0.1}$Se$_2$, (B) Co$_{0.5}$Ni$_{0.5}$Se$_2$, (C) Co$_{0.9}$Fe$_{0.1}$Se$_2$ and (D) Co$_{0.5}$Fe$_{0.5}$Se$_2$. Obviously, all of the catalysts showed agglomerated surface and fluffy cotton-like microstructure. Furthermore, when the contents of doped Fe or Ni were higher, the morphology showed more agglomerated.

Fig. S4 SEM images of (A) Co$_{0.9}$Ni$_{0.1}$Se$_2$, (B) Co$_{0.5}$Ni$_{0.5}$Se$_2$, (C) Co$_{0.9}$Fe$_{0.1}$Se$_2$ and (D) Co$_{0.5}$Fe$_{0.5}$Se$_2$. 
V LSV and Koutecky-Levich plots of Co$_x$Fe$_{1-x}$Se$_2$, Co$_x$Ni$_{1-x}$Se$_2$ and Pt/C

Fig. S5 showed LSV of Co$_x$Fe$_{1-x}$Se$_2$ and Co$_x$Ni$_{1-x}$Se$_2$ with different iron or nickel contents at different rotating rate. Obviously, the diffusion currents were enhanced with increasing rotating rate. The corresponding Koutecky-Levich plots showed good linearity at various potentials. Except for Co$_{0.7}$Ni$_{0.3}$Se$_2$ (Fig S5 (G)) and Pt/C (Fig S5 (J)) showed 4e$^-$ ORR process, other catalysts involved mixed four-electron and two-electron reduction processes with H$_2$O$_2$ as the intermediate agent.
Fig. S5 LSV curves of (A) Co_{0.9}Fe_{0.1}Se_2, (B) Co_{0.8}Fe_{0.2}Se_2, (C) Co_{0.6}Fe_{0.4}Se_2, (D) Co_{0.5}Fe_{0.5}Se_2, (E) Co_{0.9}Ni_{0.1}Se_2, (F) Co_{0.8}Ni_{0.2}Se_2, (G) Co_{0.7}Ni_{0.3}Se_2, (H) Co_{0.6}Ni_{0.4}Se_2, (I) Co_{0.5}Ni_{0.5}Se_2 and (J) Pt/C in O_2-saturated 0.5 M H_2SO_4 at various rotation rates, the Koutecky-Levich plots were shown in corresponding inset.

**ViTafel polts of Co_{x}Fe_{1-x}Se_2, Co_{x}Ni_{1-x}Se_2 and Pt/C**

Fig. S6 showed the tafel plots of the Co_{x}Fe_{1-x}Se_2 (Fig. S6 (A)) and Co_{x}Ni_{1-x}Se_2 (Fig. S6 (C)) with different iron or nickel contents, and Pt/C (Fig. S6 (E)). In addition to Pt/C, Tafel slopes of Co_{0.7}Fe_{0.3}Se_2 (110mV/decade) were smallest than others. The electron transfer number (n) and calculated kinetic-limited current density (j_k) value of different catalysts were clearly drawn in Fig. S6 (B) and (D). Co_{0.7}Fe_{0.3}Se_2 exhibited the highest j_k value of 1.83 mA cm^{-2} at 0.30 V than other Co_{x}Fe_{1-x}Se_2 and Co_{x}Ni_{1-x}Se_2 catalysts.
Fig. S6 Tafel polts of (A) Co_{x}Fe_{1-x}Se_{2} and (C) Co_{x}Ni_{1-x}Se_{2} with different iron or nickel contents at 1600 rpm, and Pt/C (E). (B, D) Electrons transfer number (n) and kinetic limiting current density (j_k) of (a) Co_{0.9}Fe_{0.1}Se_{2}, (b) Co_{0.8}Fe_{0.2}Se_{2}, (c) Co_{0.7}Fe_{0.3}Se_{2}, (d) Co_{0.6}Fe_{0.4}Se_{2} and (e) Co_{0.5}Fe_{0.5}Se_{2} and (a) Co_{0.9}Ni_{0.1}Se_{2}, (b) Co_{0.8}Ni_{0.2}Se_{2}, (c) Co_{0.7}Ni_{0.3}Se_{2}, (d) Co_{0.6}Ni_{0.4}Se_{2} and (e) Co_{0.5}Ni_{0.5}Se_{2} at 0.3V, respectively.
**LSV of Co$_{0.7}$Fe$_{0.3}$Se$_2$, Co$_{0.7}$Ni$_{0.3}$Se$_2$ and Pt/C against fuel crossover effects**

Fig. S7 showed LSV of Pt/C (A, B, G), Co$_{0.7}$Fe$_{0.3}$Se$_2$ (C, E) and Co$_{0.7}$Ni$_{0.3}$Se$_2$ (D, F) in O$_2$-saturated 0.5 M H$_2$SO$_4$ containing different concentrations of CH$_3$OH, C$_2$H$_5$OH and (CH$_2$OH)$_2$. Obviously, Co$_{0.7}$Ni$_{0.3}$Se$_2$ and Co$_{0.7}$Fe$_{0.3}$Se$_2$ exhibited strong ability to avoid ethanol and ethylene glycol crossover effects.
Fig. S7 LSV of (A, B, G) Pt/C, (C, E) Co$_{0.7}$Fe$_{0.3}$Se$_2$ and (D, F) Co$_{0.7}$Ni$_{0.3}$Se$_2$ in O$_2$-saturated 0.5 M H$_2$SO$_4$ containing different concentrations of CH$_3$OH, C$_2$H$_5$OH and (CH$_2$OH)$_2$. 